

Electrochemical Characterization of Coated Self-Piercing Rivets for Magnesium Applications

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ABSTRACT

This work reports on measurement and analysis of the galvanic interaction between steel self-piercing rivets (SPRs) having several different surface conditions and magnesium alloy substrates under consideration for use in automotive structural assemblies. Rivet surface conditions included uncoated steel, conventional Zn-Sn barrel plating and variations of commercial aluminizing processes, including supplemental layers and sealants. Coating characteristics were assessed using open circuit potential (OCP) measurement, potentiodynamic polarization scanning (PDS), and electrochemical impedance spectroscopy (EIS). The degree of galvanic coupling was determined using zero-resistance ammeter (ZRA) and the scanning vibrating electrode technique (SVET), which also permitted characterization of galvanic current flows *in situ*.

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INTRODUCTION

Self-Piercing Riveting (SPR) is an established mechanical fastening technique with a history dating over 100 years [1]. The technology gained prominence during the 1990s in the automotive industry when the manufacturer Audi adopted SPR to join body parts in its all-aluminum A8 vehicle [2], [3]. The Jaguar XJ [4], and the 2015 Ford F-150 [5] are also recent examples of the use of SPR in aluminum vehicle body construction. Steel SPRs are finding increased use in the automotive industry because they enable the joining of alternative materials which are often difficult or impossible to join using more traditional resistance spot welding. Additionally, SPR may enable the joining of mixed materials such as steel to Al [4, 6, 7, 8, 9]. The "self-piercing" aspect also allows for fastening of materials without the extra step of drilling a hole in a substrate, although it does require two-side access to the joint of interest.

Rivets used in SPR are predominately made from hardened and tempered steel in order to accomplish both the piercing function as well as having sufficient ductility to deform in order to create the clinching effect by the rivet. Boron steels permit a high degree of hardenability with only modest degrees of alloying. The rivets are generally treated with a barrier or sacrificial coating prior as part of the manufacturing process, since the typical grades of steel employed are susceptible to corrosion in an uncoated condition. However, when the rivet is used to join non-ferrous materials such as Al or Mg, the

applied coating also needs to act as a buffer to prevent galvanic coupling between the more cathodic steel and the anodic light metal being fastened. This is an inversion of the usual concern in protection of steel fasteners (i.e. where the steel of the fastener is the anode or corroding species). For the case where a nominally steel fastener is used in joining of more anodic metals (e.g. magnesium or aluminum), the approach becomes one of effectively starving the cathodic (usually hydrogen reduction) reaction occurring on the steel surface and thereby limiting the anodic dissolution of the light metal in contact. Iron and magnesium are a particularly insidious couple due to both the large differential in corrosion potentials for the dissimilar metals in a common electrolyte, but also the large proclivity for hydrogen reduction on iron surfaces in aqueous environments.

A number of studies have examined the corrosion behavior of SPRs and the impact of corrosion on the fastener performance [10, 11, 12, 13, 14, 15]. A recent project, "Magnesium Front End Research and Development (MFERD)," undertaken by the United States Automotive Materials Partnership, LLC (USAMP), with support by the U.S. Department of Energy, has emphasized the importance of understanding issues in joining Mg to itself and other materials for automotive applications [16, 17, 18, 19, 20]. Although SPRs have been identified by this project as a candidate for Mg joining, corrosion at the joint areas is an issue that has not been addressed in the a paucity of established quantitative measurement techniques has

made it challenging to assess the effectiveness of potential rivet coatings in mitigating corrosion at the interface between the rivet and the base materials. The work reported here was undertaken to explore the viability of several candidate electrochemical techniques in characterizing the efficacy of selected coating to steel SPRs and their impact on the subsequent behavior of the rivet as the cathode of a galvanic cell including adjacent magnesium alloy.

Electrochemical techniques namely open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), potentiodynamic polarization scan (PDS), galvanic corrosion (GalCorr) in zero resistance ammeter (ZRA) mode, and scanning vibrating electrode technique (SVET), were used in this work with the aim of obtaining information about the rivets, and their interaction with magnesium. OCP measurement was used to obtain information on the tendency towards reactivity/corrosivity of the rivet under study. PDS added to the information by providing corrosion rate, corrosion current density etc. EIS provided information on protective properties of coatings on the rivets. These techniques can therefore provide information during rivet selection process in their early stage before their use as a galvanic couple. SVET was used to obtain precise information of the anodic and cathodic regions along with their current density, whereas GalCorr was used to provide an understanding of the overall galvanic interaction of the rivet-Mg couple. Both SVET and GalCorr measurement are extremely useful in studying the coupling interaction between dissimilar materials.

EXPERIMENTAL

Materials

Rivets and Sample Preparation

The 5mm head diameter self-piercing rivets used in this study were produced by Henrob Corp.¹ and supplied through the United States Automotive Materials Partnership LLC (USAMP)². The rivets were made of 10B37 boron steel and heat treated to hardness of 47 RC. A micrograph of self-piercing rivet in its applied form is given in Figure 1.

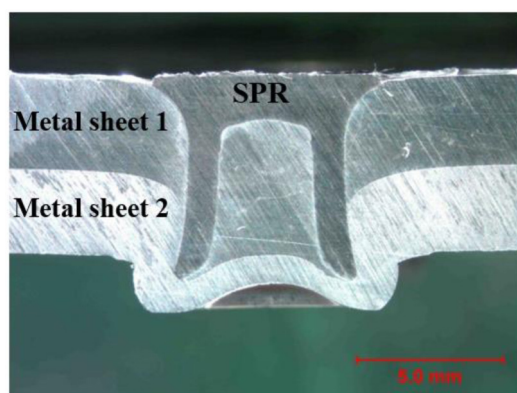


Figure 1. Micrograph of self-piercing rivet in its applied form.

Coatings

Among the four rivets studied, one was uncoated 10B37 whereas three of the rivets were surface modified/coated. The detail of the surface modifications is listed in Table 1 along with their photograph in Figure 2.

Table 1. Rivet Coating type used in this study.

S. No.	Rivet coating type	Sample Code
1	Uncoated steel rivet (10B37 boron steel)	UC
2	3 layer coating with polymeric top coat*	PC
3	Henrob Zn-Sn baseline barrel coated steel rivet	ZS
4	Ion vapor-deposited Aluminum (IVD-AI) coated steel rivet	IA

The 3 layer coating with polymeric top coat* are as follows:

1. 'AlumiPlate' electrolytic aluminum coated to 0.001" (25 microns). The AlumiPlate process is a non-aqueous electroplating of aluminum to nominal thicknesses of approximately 25 microns (Performed by AlumiPlate Inc. Minneapolis, MN, USA).
2. Henkel "Alodine® EC² TM" - electroceramic coating applied to the first aluminum layer. This is an inorganic electrophoretic coating from Henkel Corp, Madison Hts., MI, USA.
3. Henkel "29000™" sealant/topcoat applied over the EC² treatment. This is a proprietary polymer sealant from Henkel Corp, Madison Hts., MI, USA.

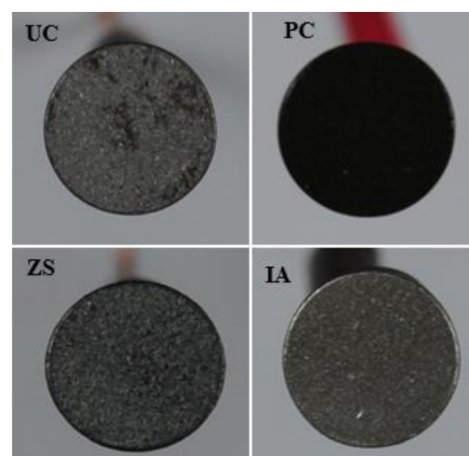


Figure 2. Experimental rivet samples a) UC b) PC c) ZS and d) IA.

The self-piercing rivets (Figure 3a) were properly masked to facilitate electrochemical measurements. The inside surface of the tubular portion of the rivet was abraded mechanically to ensure exposure of the base metal. A thin copper conducting wire was then placed coaxially with the tubular rivet shank, and completely filled with a conductive epoxy resin, purchased from MG Chemicals, Canada (CAT. No. 8331-14G, part A and part B). This ensured adequate electrical conductivity through the wire in contact with the rivet, and facilitated rivet connection to the measuring instrument. The resin was cured for 24 h. After resin cure, the neck of the SPR, extending to a certain length of the wire, was masked using a heat shrink tube. This ensured isolation of the wire and SPR/wire coupling region from electrolyte exposure (Figure 3b and 3c).

1. Henrob Corporation, 30000 South Hill Road, New Hudson, Michigan MI 48165. USA.
2. 1000 Town Center Drive, Suite 300, Southfield, MI 48075, USA.

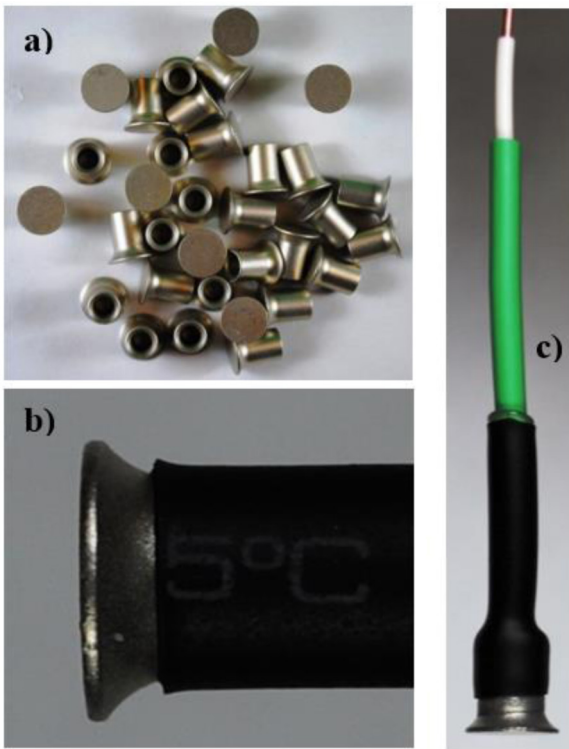


Figure 3. Self-piercing rivets displaying a) face, neck and hollow region b) heat shrink tube inserted through the neck and c) completed experimental electrode.

Magnesium

For the galvanic experiments, die-cast AM60B Mg plate was used as the coupling agent whereas Mg alloy AM30 was used for SVET experiments. For SVET, the rivet of interest was potted into a pre-machined flat piece of AM30 wrought magnesium, in order to produce a coplanar surface with rivet head and surrounding magnesium. Wrought AM30 was selected in this case for greater homogeneity in comparison to the die-cast AM60B.

Method

The following electrochemical measurements were performed on the rivet samples:

1. Open circuit measurement (OCP): rivets only
2. Electrochemical impedance spectroscopy (EIS): rivet only
3. Potentiodynamic polarization scan (PDS): rivet only
4. Galvanic corrosion measurement (GalCorr): rivet- AM60B matrix
5. Scanning vibrating electrode techniques (SVET): rivet-AM30 matrix

Electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization scan (PDS) was performed using a 3 electrode set-up as shown in Figure 4a and 4b. The SPR acted as the working electrode, a platinum mesh as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The electrolyte used was aqueous 3.5 wt. % NaCl.

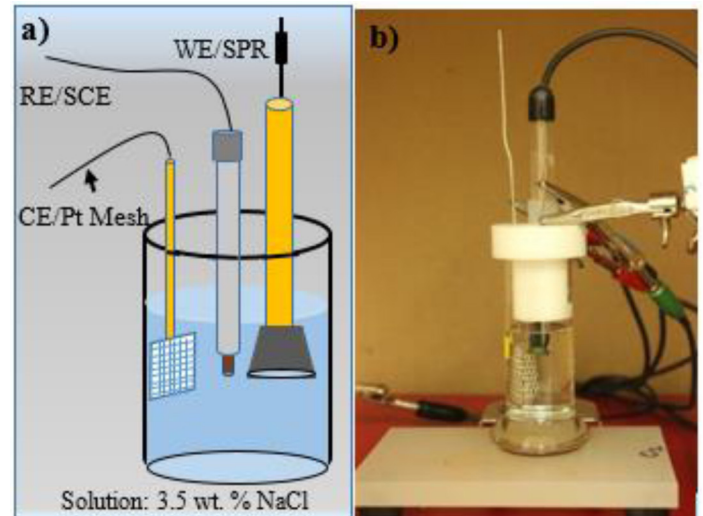


Figure 4. Three electrode electrochemical set-up a) schematic representation and b) pictorial representation, for OCP, EIS and PDS measurements.

An IFC 1000 Potentiostat/Galvanostat/ZRA, from Gamry Inc.³ was used for the electrochemical measurements. Data were acquired using Gamry Framework™ software version 6.21. A Perspex™ cylinder mounted on a non-reactive plastic board and clamped with an O-ring insert was used to hold the electrolyte, aqueous 3.5 wt. % NaCl. For the EIS measurement, impedance response from 10^{-2} Hz to 10^5 Hz was measured and the data were acquired at the rate of 10 points per decade. In EIS a small AC potential perturbation, typically a sine wave of amplitude $\sim \pm 10$ mV is applied on a system with respect to its open circuit potential over a wide range of frequency (typically from 10^{-5} - 10^{-2} Hz) and the response of the current is measured at each frequency. Barrier properties, water uptake and diffusion rate of organic coating, or the various processes involved during corrosion can be obtained [21, 22, 23, 24, 25, 26].

PDS scans were performed by scanning the potential of the working electrode from -0.5 volts to $+1.5$ Volts with respect to the open-circuit potential (OCP) at a scan rate of 1 mV/sec. In PDS, the potential of the working electrode is scanned at a selected rate over a relatively large potential range by applying a current through the electrolyte. It is a very commonly used testing technique for measuring corrosion resistance, corrosion current density, etc. of metals.

The experimental arrangement for the galvanic corrosion measurements consisted of two compartments separated by a salt bridge as shown in Figure 5. One compartment was a glass beaker filled with the electrolyte of interest (aqueous 3.5 wt. % NaCl) into which the shrouded SPR assembly was immersed as working electrode 1 (WE-1), as well as the saturated calomel reference electrode (SCE). The second compartment consisted of a die-cast magnesium plate (AM60B) as working electrode 2 (WE-2) mounted with a Perspex™ cylinder and clamped with O-ring insert to hold the electrolyte. An agar salt bridge was used to connect the two compartments. Salt bridge completes the electrical circuit, maintain charge balance and allow the cell to function. The experiment was performed in the zero resistance ammeter (ZRA) mode.

3. Gamry Instruments Inc, 734 Louis Drive, Warminster, PA 18956, USA

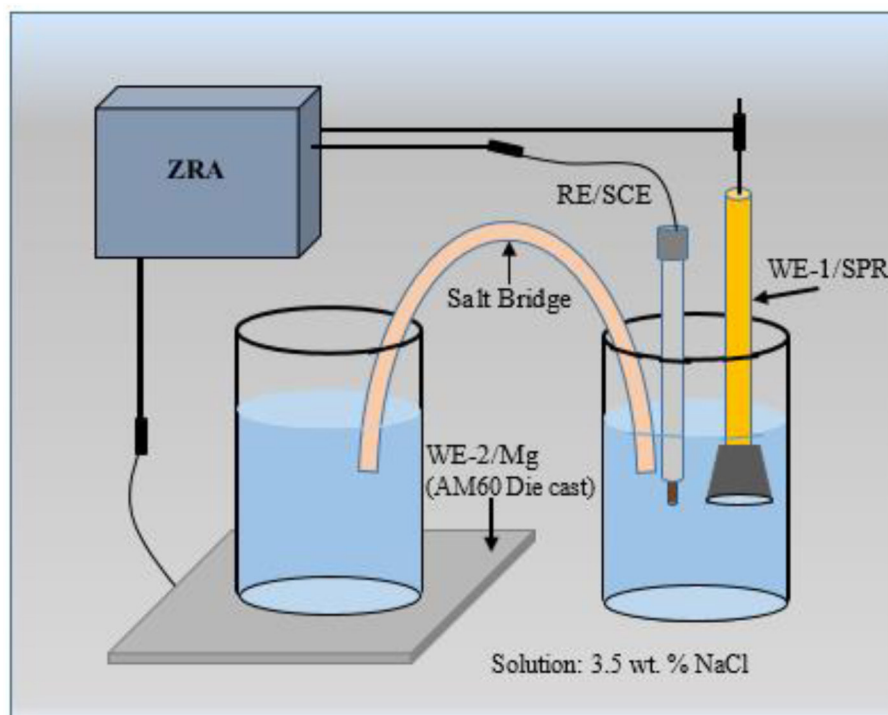


Figure 5. Schematic set-up of galvanic corrosion measurement.

potentiostat previously described. The ZRA mode ensures that the two working electrodes (WE-1 and WE-2) behave as if they were directly connected by a 'zero-resistance' wire, such that the galvanic current between cathode (rivet) and anode (magnesium), and potential can be measured/recorded. Material loss rate at the anode can be then determined by application of the Faraday law once the current flow is measured.

In a largely different style of experiment involving the coated rivets and their galvanic interaction with surrounding magnesium, the scanning vibrating electrode technique (SVET) was employed, permitting an "*in situ*" determination of the coupling between any particular rivet and adjacent magnesium as might be encountered in an actual riveted joint. For these experiments, however, the rivets as acquired were mechanically pressed into pre-drilled holes in the substrate of interest - magnesium alloys, in this case. This technique uses a vibrating probe/electrode to scan the sample surface that detects the gradient in ohmic potential produced by local currents generated from actively corroding surfaces immersed in the electrolyte. From the variation in potentials, areas of varying current densities can be located and measured. Details of the SVET methodology can be found elsewhere [27, 28, 29].

SVET experiments were performed to measure the current density distribution between the rivet head of interest and surrounding magnesium for the geometric situation illustrated in Figure 6 (a), throughout the volume defined by the bi-metal/electrolyte interface at its free corrosion potential (i.e. there were no externally applied potentials). The SVET instrument used in these experiments was purchased from Applicable Electronics, USA⁴. The scanning probe

was a Pt-Ir microelectrode with a 10 μ m diameter tip that was platinized to a 20 μ m sphere. A 2D schematic of the SVET process is shown in Figure 6a. The probe was placed 150 μ m above the sample surface and vibrated with an amplitude of 20 μ m along the X and Y direction. A pair of platinized Pt wires were used as a reference and bath ground electrode respectively. Scans were initiated immediately after immersion in an equal volume mixture of 0.05 wt. % NaCl and 0.05 wt. % MgSO₄. This particular solution, determined after a number of trials, displayed less corrosivity for the rivet-Mg couple under study, when compared to electrolytes of higher ionic concentration where the galvanic reaction was vigorous with copious hydrogen evolution, and wherein the SVET measurements were difficult due to this disruption. For the results illustrated here, the defined probing area included a matrix of 20 $\times$ 20 individual point measurements within an approximately 3 $\times$ 3 mm field, wherein a scan of the entire data field lasted approximately 6 minutes. Two such scans were performed, with an 80 minute interval between. The experimental probing arrangement for the rivet and surrounding magnesium is illustrated in Figures 6 (b) and 6 (c), and consisted of portions of the rivet head and adjacent magnesium. Figure 6 (c) illustrates the image of the probed array seen through the instrument microscope, with overlay image of the probe locations in the test array. Areas of the galvanic couple that were isolated from contact with the electrolyte were defined using a combination of acetate solution (e.g. nail polish) with carefully overlaid transparent tape. This then confined the volume of measured activity as well as the insulating boundary conditions for electric fields generated by the couple.

4. 22 Buckingham Drive, Sandwich, MA 02563, USA. <http://www.applicableelectronics.com>